13

RADC-TR-77-52
Semi-Annual Technical Report No. 5
January 1977

TECHNOLOGY AND PHYSICS OF INFRARED AND POINT CONTACT DIODES

Department of Physics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Sponsored by
Defense Advanced Research Projects Agency
ARPA Order No. 2618

ROME AIR DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
GRIFFIS AIR FORCE BASE, NEW YORK 13441

TECHNOLOGY AND PHYSICS OF INFRARED
AND POINT CONTACT DIODES

Contractor: Massachusetts Institute of Technology
Contract Number: F19628-74-C-0182
Effective Date of Contract: 24 January 1974
Contract Expiration Date: 28 February 1977

ARPA Order No.: 2618
Program Code Number: 5D10
Period of Work Covered: 1 May 1976 - 31 October 1976
Principal Investigator: Ali Javan
Phone: 617-253-5088
Project Engineer: Dr. Audun Hordvik
Phone: 617-861-4927

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

This report has been reviewed by the RADC Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public including foreign nations.

This report has been reviewed and is approved for publication.

APPROVED:

R. H. Picard for
AUDUN HORDVIK
Contract Monitor

Do not return this copy. Retain or destroy.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER RADC-TR-77-52	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Technology and Physics of Infrared and Point Contact Diodes.		5. TYPE OF REPORT & PERIOD COVERED 5/1/76 - 10/31/76 Scientific Interim
		6. PERFORMING ORG. REPORT NUMBER Semi-Annual Tech.
7. AUTHOR(s) Ali Javan		8. CONTRACT OR GRANT NUMBER(s) F19628-74-C-0182, ARPA Order-2618
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics Mass. Inst. of Tech., Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2001J01-01 61101E
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Proj. Agency - 1400 Wilson Blvd. Arlington, VA 22209		12. REPORT DATE Jan. 1977
		13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Deputy for Electronic Technology (RADC(ETSL)), Hanscom AFB, MA01731 Contract Monitor: Audun Hordvik		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Semiannual technical rept. no. 5, 1 May - 31 Oct 76,

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18p.

18. SUPPLEMENTARY NOTES

This Research was sponsored by the Defense Advanced Research Projects AGency, ARPA Order 2618

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Tunneling resonances, dielectric formation, oxide studies, photoemission.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Masks were obtained to make the far infrared holographic antenna/diode array which had been designed earlier. Fabrication parameters were investigated, and a procedure was established. Electrical characteristics of the junctions are described. Most good

over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

401 735

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Cont. Block No. 20 microvolts

arrays are matched in resistance within a factor of two. About 20 μV of rectified voltage was obtained from one of these early junctions with far infrared radiation focused on the antenna.

The liquid helium dewar required repair twice, and the flexible transfer tube was repaired once during this half year.

Response of Al-Al_2O_3-Pb junctions to visible laser radiation at liquid helium temperature has been studied. We have shown that focusing on the Al stripe produces a bolometric effect, whereas the junction gives a very structured response but only at biases less than 20mV. Second and third order mixing have been observed at microwave frequencies in preparation for looking at near infrared mixing. Preliminary attempts to observe second order mixing between two spatial modes of a 1.15μm He-Ne laser were unsuccessful. Junctions have been fabricated with a semitransparent lead layer which became superconducting at liquid helium temperature.

Attempts to observe negative resistance in Sn-SnO-Pb junctions were frustrated by junction damage during the process of soldering test leads to the contact pads. A sample was successfully prepared with pre-attached leads, and peaks due to both superconductors were observed; but at no time was negative resistance actually observed. Attempts were made to use vanadium (V) with lead as the superconductors; insufficient V was evaporated each time.

A point contact mixer assembly for adjustment and use at liquid helium temperature has been designed and fabrication begun.

Two patents covering optical addressing of high speed memory devices were refiled with the U.S. Patent Office, and patents were filed in Germany and Japan.

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

TABLE OF CONTENTS

1. SUMMARY

Masks were obtained to make the far infrared holographic antenna/diode array which had been designed earlier. Fabrication parameters were investigated, and a procedure was established. Completed junctions are described electrically. Most good arrays are matched in resistance within a factor of two. About 20μV of rectified voltage was obtained from one of these early junctions with far infrared radiation focused on the antenna.

The liquid helium dewar required repair twice, and the flexible transfer tube was repaired once during this half year.

Response of $Al-Al_2O_3-Pb$ junctions to visible laser radiation at liquid helium temperature has been studied. We have shown that focusing on the Al stripe produces a bolometric effect, whereas the junction gives a very structured response but only at biases less than 20mV. Second and third order mixing have been observed at microwave frequencies in preparation for looking at near infrared mixing. Preliminary attempts to observe second order mixing between two spatial modes of a 1.15μm He-Ne laser were unsuccessful. Junctions have been fabricated with a semitransparent lead layer which became superconducting at liquid helium temperature.

Attempts to observe negative resistance in Sn-SnO-Pb junctions were frustrated by junction damage during the process of soldering test leads to the contact pads. A sample

was successfully prepared with preattached leads, and peaks due to both superconductors were observed; but at no time was negative resistance actually observed. Attempts were made to use vanadium (V) with lead as the superconductors; insufficient V was evaporated each time.

A point contact mixer assembly for adjustment and use at liquid helium temperature has been designed and fabrication begun.

Two patents covering optical addressing of high speed memory devices were refiled with the U.S. Patent Office, and patents were filed in Germany and Japan.

2. INTRODUCTION

Preliminary work in this laboratory has shown that tunneling characteristics of metal-oxide-metal junctions are essentially independent of frequency as long as photon energy is less than the barrier height. Recent calculations show the effects of circuit parameters on response of antenna/diode combinations; the junction capacitance is responsible for roll off in the infrared. Capacitance reduction requires shrinking junction size, hence the need for micron and submicron geometrics. Photoemission (over the barrier rather than tunneling) and thermal effects dominate the response in the visible region.

Important elements of device merit are junction non-linearity and negative resistance. These are being demonstrated in small, high-speed junctions capable of operation in the infrared. The effects may be further enhanced by choice of materials, techniques of application, and operating temperature.

3. FOUR ELEMENT HOLOGRAPHIC ARRAY

Our first set of masks for the four element infrared holographic array were delivered in May (Fig. 1). Careful inspection demonstrated excellent pattern registration. The thin tips that cross to form the rectifying junctions are 2.5μm wide, promising a potential 6.3μm^2 junction area if exposure and development do not enlarge these patterns. A metal lift process is used in which the metal is evaporated on top of a photoresist with a pattern of holes through to the substrate. When the resist is "stripped," the overlying metal is also removed. The photoresist being used was Shipley 1350 B and later in the period 1350 J. These are positive resists and it is the exposed areas that are subsequently taken off by the development process. Fortunately an exposed area develops its broadest opening near the substrate, thus producing an "overhang" separating the metal in the hole from that on top of the resist and assisting in the removal of the extraneous resist and metal. Resist exposed through narrow slits in the mask will become slightly larger with overexposure, and yet an underexposed pattern may not be open completely to the substrate. Masks pick up resist from the substrate and become dirty and unusable. For top quality over the whole mask, less than five exposures are usually possible. With some degradation as many as fifteen exposures are sometimes possible. A new

set of ten masks has been ordered and received.

Considerable efforts were made to establish correct surface preparation for glass and quartz substrates. Preparation now consists of: (1) scrub surface with alkanox and water, rinse throughly with water and blow dry, (2) immerse for 10 minutes in chromic-sulfuric acid cleaning solution heated to about 100°C, (3) rinse in demineralized water for 3 minutes and blow dry, (4) bake 15 minutes at 185°C, and (5) cool to room temperature just before applying the photoresist. Hot nitric acid and rinse just before baking tended to make the subsequent metal deposition less adherent. Omission of the alkanox or the chromic-sulfuric caused radical reduction in adherence. The bake is also essential, but excessive time again reduces adherence; this may be associated with a softening of the glass surface as indicated by ease of surface scratching with tweezers.

Initial photoresist work was done with Shipley AZ 1350 B, a thin, positive resist. After conversation with the manufacturer we converted our process to AZ 1350 J which contains the same polymer, but with less solvent. The result is a thicker film giving better separation of the film on the substrate from that on the resist. Some difficulty was experienced of erratic edge definition. So a black anodized aluminum chuck was made for the mask aligner, to prevent reflections off the chuck through the (transparent) substrate from expos-

ing resist. This problem did not re-appear although there is reason to suspect that a more significant factor was improved technique in use of the photochemicals. The AZ 350 developer is diluted with water before use and must be thoroughly mixed (shaken) just before resist development. When this is not done considerable edge peeling occurs. In our process we find 40 second development close to optimum.

Substrate baking after development and before placing in the evaporator was tried initially, but considerable difficulty was encountered in stripping the resist. Currently we blow substrates dry and then put in the evaporator. Some experimentation was conducted to optimize time in the evaporator prior to glow discharge cleaning and evaporation, but no true optimum was found between three and twenty hours. Glow discharge is conducted in an atmosphere of 200 μm of oxygen in the valved off bell jar. A current of 2mA is run from the negatively charged aluminum discharge ring placed below the substrates. A time of 10 minutes is currently used although this does not appear critical, nor does the current. After re-pump down the chromium is evaporated. Freshly broken chromium is evaporated from a tungsten basket. The chromium is quickly outgassed onto the shutter and the bell jar re-pumped before evaporation proceeds. About 300 Å of chromium are evaporated and 400 Å of nickel. Excess

heating during evaporation makes the resist very difficult to remove, and invariably some of the metal in the exposed areas is also removed. Attempts to increase nickel have led to poor edge definition, probably due to excess resist curing rather than the thicker metal, which is considerably thinner than the resist. Filament-substrate distances have been adjusted to reduce heating during evaporation. It is not clear that our current eight inch spacing is better than a larger one.

Stripping is done in Remover 1112A at room temperature followed by a 10 minute 95°C bake before second photoresist. The second metalization is significantly different from the first in that the glass surface has now been wet without a subsequent high temperature bake. Whether a vacuum dry or a longer pre-resist bake is desirable will depend on the operational characteristics of the nickel oxide produced.

As in any process involving a large number of interrelated variables, the best solution generally will not be found by optimizing operations individually.

Most junctions have resistances in the desirable range of 200 to 1000Ω, and within arrays of four diodes the largest resistance is usually less than twice the smallest. In one case all four were within 12% of a mean value. About 20 μV of rectified voltage was obtained from one of the first junctions exposed to the HCN laser (337 μm).

4. REPAIR OF CRYOGENIC EQUIPMENT

The liquid helium dewar was returned to the manufacturer twice during these six months for repairs. He found and repaired three leaks the first time and two the second. We seem to have a corrosion problem and will attempt to prolong the life of the dewar by keeping it dry when not at low temperature.

The flexible helium transfer tube also developed a leak and was repaired.

5. LOW TEMPERATURE RESPONSE OF $Al-Al_2O_3-Pb$ JUNCTIONS

The offset signal at bias greater than 20 mV was discussed in the previous report. Its cause has been sought and found in the period of this report. Early observations indicated that the low bias (structured) signal was optimized by focusing the laser at a different point than the optimum for the offset at higher bias. Ultimately it was demonstrated that there is a definite response obtained by focusing the laser on an alumimum line which accounts for the observed offset. The junction response is restricted to the low bias region associated with tunneling between the superconductor and the normal metal. This has been quenched at fields of 1250g and partially quenched at lower fields.

Several experiments have been performed in preparation for a third order visible mixing experiment which we have

proposed using Al-Al_2O_3-Pb (superconducting) junctions. The size of the desired beatnote should be the same order of magnitude as that arising from mode beating of the 1.15 μm laser itself. An early attempt to observe this mode beating was not successful. We then decided to study the system at lower frequencies and sought beatnotes from third order mixing between two 9 GHz klystrons and an rf source. This observation was successful but attempts to achieve greater sensitivity by using an rf preamplifier (50 Ω input impedance) demonstrated the necessity of lowering the junction impedance to the same range. The same beatnotes have been observed, with high sensitivity, using junctions of about a hundred ohms impedance and our low noise preamplifier. We are now in a position to re-examine the mode beating of the 1.15 μm laser. A PZT pusher has been installed on this laser to facilitate continuous tuning between spatial modes separated by the measured 150 MHz when we perform the third order laser mixing.

Mixing was observed in Pb-Al junctions cooled to 2.1 K, biased at a voltage on the order of the energy gap of Pb, e.g. ∿1mV. Second order mixing involved detection of zero beat at $\nu_1 \cong \nu_2 = 9.00$ GHz. The detected signal was roughly the same magnitude as the rectified signal from either ν_1 or ν_2, which is predicted. Signals were ∿40 μV pp. This beat note responded to bias in the predicted way, e.g. was

zero at $V_b = 0$, maximum at $V_b \approx$ 1mV, and zero at higher bias.

Third order mixing was achieved using

$$\nu_1 = 9.000 \text{ GHz}$$

$$\nu_2 = 9.100 \text{ GHz}$$

$$\nu_3 = 100 \text{ MHz}$$

The zero beat note maximized at zero bias, was zero at V_b=1mV, and had a nonzero value for larger biases. As predicted, the zero beat showed a maximum for a specific ν_3 power.

The junction resistance at large bias was ∿500Ω; at the superconducting transition, the resistance was 6000Ω. This is the "dynamic" junction resistance at the bias level which maximizes the 2nd order response.

With another junction the frequency response of a 400μm^2 area junction was tested by varying the second order beat note from zero Hz to ∿200 MHz. No overall decrease in signal level was observed, although line inductance caused bands of filtering at 19 MHz, 142 MHz, and 168 MHz to occur. This response was compared to a 2500 μm^2 area junction response. Here, the junction seemed to stop responding at ∿32 MHz. It was not determined whether it responds at much higher frequencies.

Second order mixing of two spatial modes of the 1.15 μm He-Ne laser was attempted using several "good" junctions.

The radiation was coupled through the thin Al. However, it became apparent that with an amplifier input impedance of 50Ω, the Al lead resistance must be very low to observe the beat signal unattenuated.

A semitransparent Pb film that is electrically conducting became superconducting at 4°K. The underlying Al lead was made about 2000 Å thick. Junctions of this design have been made with about 100Ω junction resistance with less than 15Ω in series. These will be used in future mixing studies.

6. LOW TEMPERATURE LEAD-TIN JUNCTION

Several low temperature runs were made with lead on tin. These are very fragile junctions and are easily destroyed by soldering to the substrate even with indium. Attempts to solder leads with gallium using a piece of copper wire as a soldering iron at body temperature met with limited success; gallium, just above its melting point does not wet copper or gold well. In every case, leads came off the substrate preventing junction measurement by the time that helium was superfluid. One indium soldered junction had I-V bumps indicating a negative resistance partly shorted by junction defects (apparently induced by heating the substrate while soldering). A junction was fabricated after leads were attached to the pads and the leads later connected to the holder. The display was generally as expected, but the pattern was not sufficiently convoluted to show negative resistance. This approach will be tried again.

7. OTHER SUPERCONDUCTIVE WORK

Superconductive energy gaps were calculated at several temperatures and several combinations were found that give ratios of about two in energy at temperatures between two and four degrees K. These include Pb-V, V-Ta, V-Sn, and Pb-Sn.

Vanadium was obtained and several unsuccessful attempts were made to evaporate sufficient vanadium to make a lead on a vanadium junction. Vanadium evaporates at a considerably higher temperature than any other material we have evaporated in this laboratory.

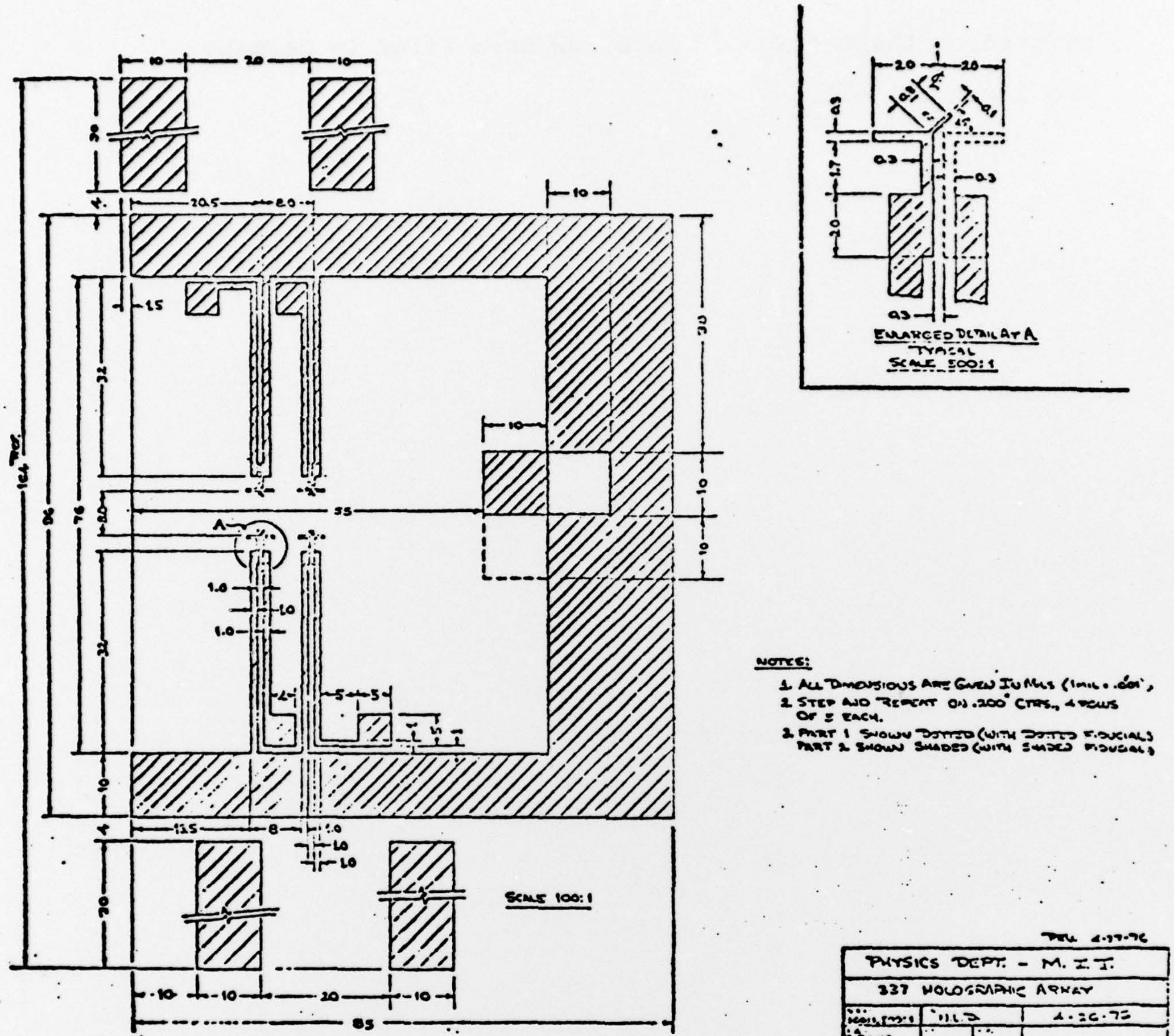
8. LOW TEMPERATURE POINT CONTACT

A point contact mixer assembly for adjustment and use at liquid helium temperature has been designed and fabrication started. This will be used for observing mixing in the small area junctions possible with a point contact between a superconductor and a normal metal. Results will be compared with those obtained from similar "printed" structures.

9. PATENTS

Two patents covering optical addressing of high speed memory devices were returned by the U.S. Patent Office with comments. These comments were acted on and the patents re-filed with slightly modified claims this summer. Patents

written on these concepts have now been filed in Germany and Japan as well.



Drawing for 337 μm four bit holographic array.